Zirconium and Iron Densities

in a Wide Range of Liquid States[1]

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

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ABSTRACT

Metals (Fe, Zr) were investigated under 1bar air ambient atmosphere. Electrical pulse current during 5-7 microseconds heated iron and zirconium wires. Wires were shadowgraphed by a pulse laser with the duration of $\tau \approx 6$ nsec. The shadow picture was transmitted to a digital CCD-camera and then subjected to digital photometrical procession.

The differences between our measured and known literature curves for liquid iron density consist of 1-6%. It reveals that a new method is valid. The dependencies of resistivity against specific imparted energy were obtained for liquid state of Fe and Zr. As the examples of iron and zirconium, a possibility of using the proposed method to obtain reliable data on thermal expansion of liquid metals and its electrical resistivity over the wide range of the liquid phase is demonstrated.

KEY WORDS: density, expansion, fast heating, high temperature, iron, liquid state, resistivity, zirconium.

1. INTRODUCTION

The measurement of time dependence of a liquid metal thermal expansion value is done at the electric current pulse heating of wire specimens up to the temperatures much higher the melting point. The way to obtain the liquid metal is to heat up a cylindrical rod (wire) of 100 to 200 μm in diameter (d) with an electric current pulse ($d<<l$, where l is the wire length). During the period of heating the wire in the liquid phase expands laterally, but not longitudinally for it was fixed at the ends.

A shadow picture of the wire diameter is measured by digital CCD-camera at exact time delay. Duration of a laser pulse shadowgraph τ_p while being measured by digital video camera, is determined by a minimum temperature interval of measurements and temperature increment rate (in our case the temperature increment rate is $\approx 10^{10}$ $K \cdot sec^{-1}$; thus, $\tau_p \approx 10$ nsec corresponds to the temperature interval of 10 K).

2. METHODS

2.1. Optical Scheme of Measurement Method

The optical scheme of measurements is as following. The surveyed area is shadowgraphed by a second harmonic pulse Nd:YAG laser with the radiation wavelength of λ = 530 nm and duration of 6 nsec. The surveyed object is wire of 200 μm in diameter (steel) and 180 μm in diameter (Zr), and length of 30 mm. It was heated with an electric current pulse of 5 to 7 μsec in duration. The shadow picture of the wire was transmitted to a digital CCD-camera input with a magnification of 10 power. A narrow band interference filter and a set of colour and neutral light filters suppressed thermal radiation of the heated wire. The synchronisation unit synchronised current and laser pulses to CCD-camera, and provided for a variable time delay of the shadowgraph over the current heating pulse.

Fig. 1 shows a characteristic picture obtained through the digital video camera. Spatial resolution of the CCD-camera along the axis of abscissas (lateral dimensions of the wire) is 6 μm (size of the pixel).

Since the magnifying factor is 10 power the spatial resolution at the object is about 0.6 μm. It is greater than the laser pulse shadowgraph wavelength and the optical system is capable of providing for such resolution. The assessment of the results has shown that it is possible to process image dimensions with the error of nearly 1 μm.

2.2. Current Heating Method and Measurement of Imparted Energy Value

The capacitor bank with stored energy of 25 kJ was discharged through the specimen and ballast resistor connected in series. To measure the total current running through the wire the Rogovsky coil was used. The procedure to calibrate the Rogovsky coil implied recording of current (with amplitude of up to 10 kA) running through the current shunt with known parameters (impedance 0.03 Ω, inductance 0.12 nH) and comparison of signals at the current shunt and Rogovsky coil using a digital oscilloscope Tektronix754C. A deviation of conversion coefficient of the Rogovsky coil constant did not exceed 1.5% in the area where the current change rate did not exceed $5 \cdot 10^9$ A/sec within 10 microseconds of the current run. To measure voltage across the specimen the voltage divider is used. The attenuation was determined with the accuracy of 0.1% with regard to direct current.

To record a laser pulse the photoreceiver was used. The basic components of the photoreceiver is the silicon PIN-photodiode with quartz-quartz optical fibre. The photoreceiver rise time was less than 10 nsec, and the dynamic range was 600 at 0 –50 MHz. The maximum deviation from linear dependence of the voltage output signal from the radiation input signal was less than 5% over whole dynamic range of

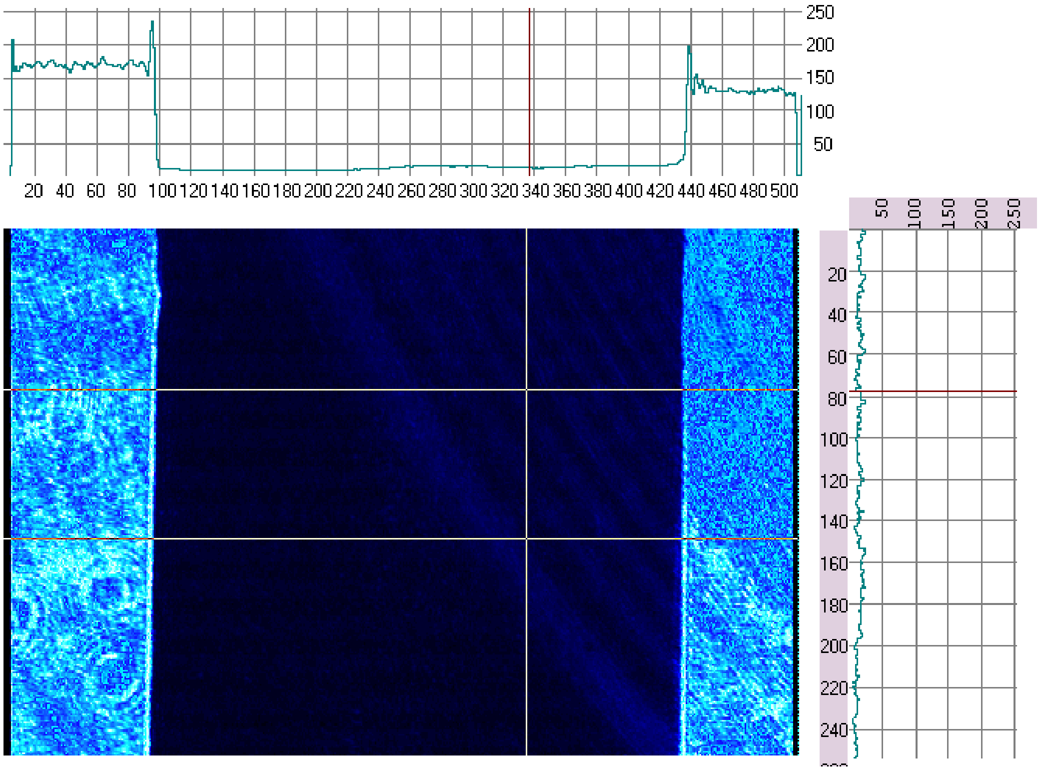

Fig.1.

Image of wire diameter (0.2 mm), horizontal axes, on CCD -camera.

Above is shown the dependence (arbitrary units) – digital photometrical processing of the shadow picture across the wire. Right-hand dependence (arbitrary units) – digital photometrical processing of the shadow picture along the wire.

photoreceiver.

A wire piece of about one meter length was determined with the error of about 0.1%. The mass of the specimen can be measured with accuracy of about 0.5%. The specimen was weighted in air and in boiled water to give the result in density - 6.505 g/cm^3. The electrical resistance of a specimen was determined by formula:

$$R(t) = [U(t) - L(dI/dt)]/I(t)$$

where U is the voltage at the specimen, L is the inductance of the specimen, I is the current running through the specimen. The calculation of the specimen inductance L gives the value measured within 13% when the specimen's volume increases twice. A total error value of R determining will be 3% for the case dI/dt $\leq 10^9$ A/sec. The electrical resistivity of metal is calculated by: ρ(t) = R (t) S/l, where S is the cross-section of the expanding specimen, l is the specimen's length. The amount of the energy E absorbed per unit of mass will be:

$$E(t) = \int_0^t [I^2(t) \cdot R(t)/m]dt$$

where m is the mass of the specimen. A possible error of determining of E is about 4% near the melting point. The absolute error of measurement of the heated wire diameter (d) by a CCD-camera was 1 μm (without processing of the image edge diffraction picture). Taking into account that the volume is proportional to d^2, a measurement error of the expanded specimen diameter (volume) will be 1.4 μm.

The composition in mass percents of the wire of 0.18 mm in diameter is: Fe, Hf, O_2 – 0.05% each; Nb, C, - 0.03% each; Al, Si, Ti, Cu – 0.005% each; N_2 – 0.01%.

3. MEASUREMENTS ON LIQUID IRON

3.1. Experimental results

The measurement methodology was tested using iron specimens (steel with carbon content of about 0.1%). Wire was of 200 μm in diameter. The diameter of wire and the iron density were determined as to the verified methodology. A specimen of about 1 meter length was weighted on the analytical balance (with an error of 0.15 mg) first in air, and then in the boiled water. The measured initial density of iron appeared to be 7.87 g/cm^3. The length of the specimens subjected to heating was 30 mm (with accuracy of up to 50 μm). Fig. 2 provides for a measurement result of an expansion of iron wire obtained with 16 specimens. Each specimen is represented by a square dot in Fig. 2.

Fig. 3 provides for the results of measurements of liquid iron density against the specific imparted energy E.

According to our data (Fig.2-3) the average temperature coefficient of volumetric expansion of liquid iron from melting point 1810 K to boiling point 3148 K [2] (at ≈ 2.5 kJ/g) is equal to ~102×10^{-6} K^{-1}. Last value is close to the data of Fe [3] ($\beta = 91.5\times10^{-6}$ K^{-1}, linear up to 2300 K), and to the data of [4] ($\beta = 115.1\times10^{-6}$ K^{-1} for liquid steel with 0.12% C).

3.2. Experimental procedure for the calculations of one shot (Fe-18).

As an example of how this methodology was used to obtain electrical resistivity of liquid iron we provide for several figures illustrating one of the experiments (Fe-18).

Fig. 4 gives the values of current and voltage at the specimen and a laser flash, shadowgraphed just at the moment, when the melting was finished (at the imparted energy of 1.33 kJ/g).

Fig. 5 shows the result of calculation as the reduced electrical resistivity ρ^0 (referred to

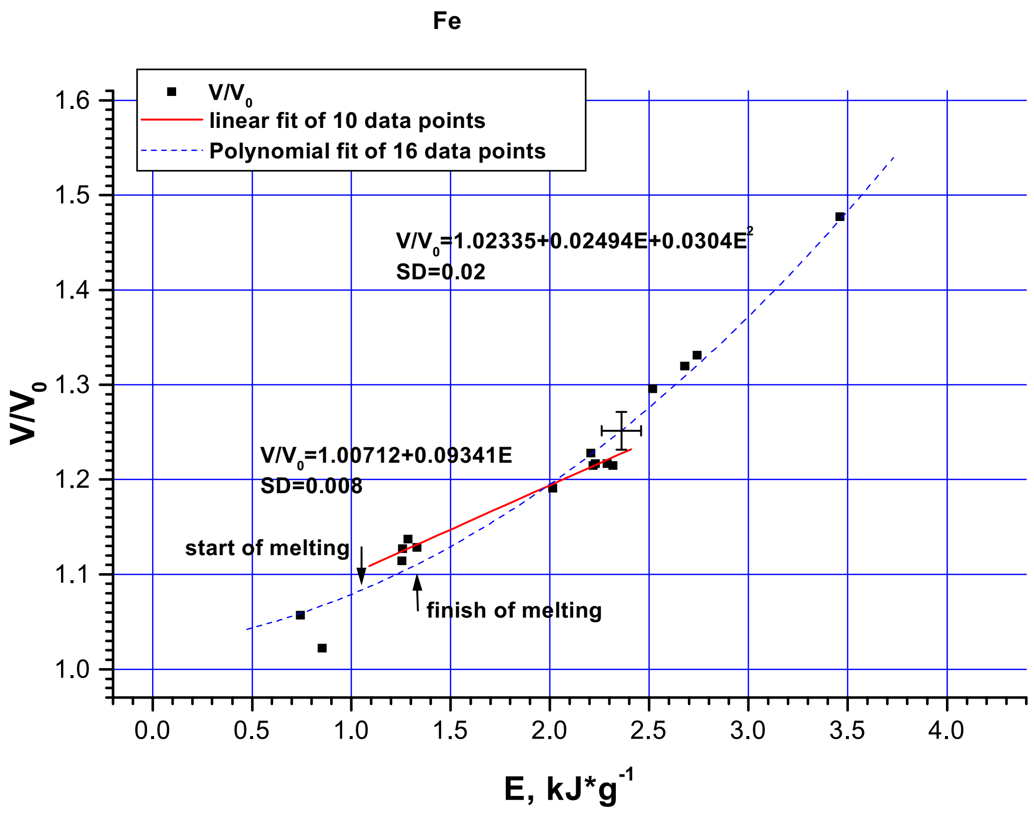

Fig.2

Thermal expansion of Fe against specific imparted energy.

The start (1.06 kJ/g) and the end (1.33 kJ/g) of iron melting are shown with arrows according to [1]. Square points – our data. Dashed curve – polynomial fit over all 16 data points. Solid curve – linear fit of the data in a narrow liquid phase region (10 points).

The axis of ordinates represents the relative change of volume V/V_0, and the axis of abscissa represents the specific imparted energy E (starting from the room temperature level). The error of specific imparted energy and volume change is given for one of the imparted energies (close to 2.5 kJ/g).

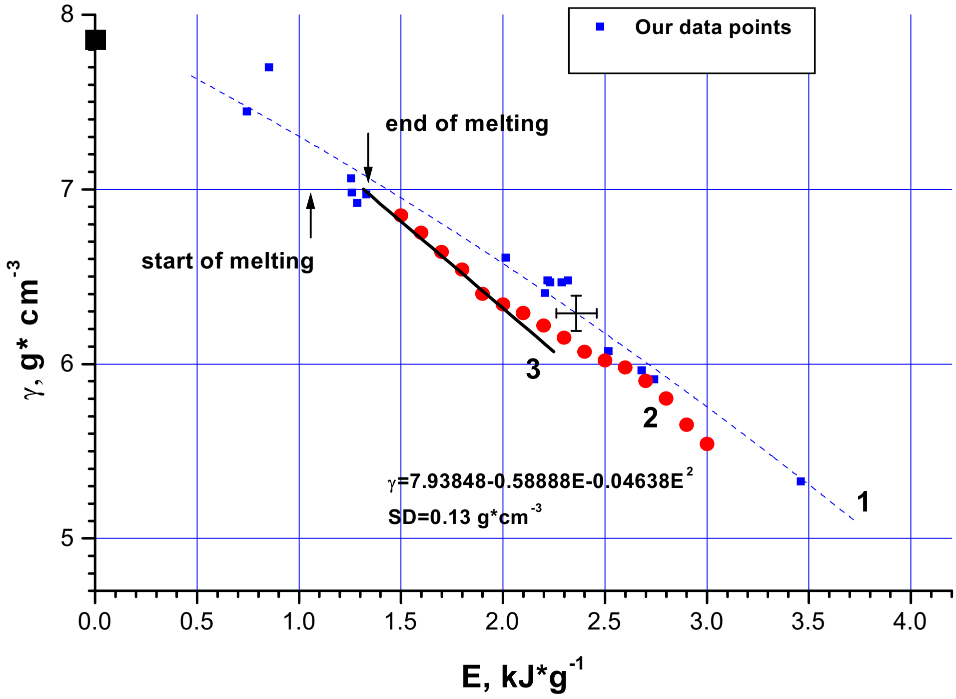

Fig.3

Density of Fe against specific imparted energy.

The start (1.06 kJ/g) and the end (1.33 kJ/g) of iron melting are shown with arrows according to [1]. Square points – our data, initial point is shown under E = 0. Dashed curve – polynomial fit of all our data. The error of density and imparted energy measurement is given for the value close to 2.5 kJ/g.

Dashed curve 1 - our data for solid and liquid iron, obtained in air. The full time of heating - 10 microseconds.

Circle points 2 - data of [5] for liquid iron, obtained under high argon pressure (2 kbars). According to [5] E = 3 kJ/g corresponds to 3950 K.

Solid line 3 - data of [6] for liquid iron, obtained in water under high pressure (up to 3.8 kbars). The full time of heating in [6] - 55 microseconds. According to [6] E = 3 kJ/g corresponds to 3861 K, (accordingly: E = 3.75 kJ/g – 4770 K).

the specimen dimensions at room temperature) as the specific electrical resistivity ρ, for which the thermal expansion with regard to the experimental data on 10 specimens shown on Fig 2 was taken into account. At melting point (E = 1.33 kJ/g) the ρ equals to $\rho^0 \times V/V_0$, where the increase in volume by 13% is taken into account according to the linear fit of data given in Fig. 2. Density of liquid iron is 6.95 g/cm^3 (linear fit near melting point, Fig.2) or 7.05 g/cm^3 (polynomial fit of all our data, Fig.3) under our measurements for end of melting.

Electrical resistivity of liquid iron against temperature may be obtained. Taking into account the heat capacity of liquid iron as a constant C_p = 0.786 J/g·K [2, 5] one can obtain electrical resistivity of liquid iron ~150 μΩ*cm at the boiling point 3148 K [2] at imparted energies ≈ 2.5 kJ/g. Under maximum imparted energy (3.5 kJ/g), there was seen in the photography unlevelled edge of the liquid iron cylinder. Perhaps it was connected with the iron boiling under evaluated temperature T = 4500 K.

3.3. Review on density measurements of liquid metals (Fe and steel)

The well-known book by Wilson [2] gives the value of electrical resistivity of the liquid iron at the melting point as 138.6 μΩ cm. The heat capacity of the liquid iron is C_p = 0.786 J/g·K [2].

In case of liquid steel with a carbon content of 0.13%, the formulas to calculate electrical resistivity at the temperatures up to 1923 K are given in [4]:

$\rho = 135.1[1+2.88 \cdot 10^{-4}$ (T-1810K); $\rho = 145.5[1+3.14 \cdot 10^{-4}$ (T-1810K)

Experimental data on liquid iron had been obtained in [6] by a 55-microseconds electrical pulse heating. Iron wires were heated in water, under high pressure (up to 3.8 kbars). Authors [6] gave data up to 4770 K (E = 3.75 kJ/g), but density was obtained only to 2952 K (E = 2.25 kJ/g), see Fig.3. Specific heat capacity is 0.825 kJ/g*K [6].

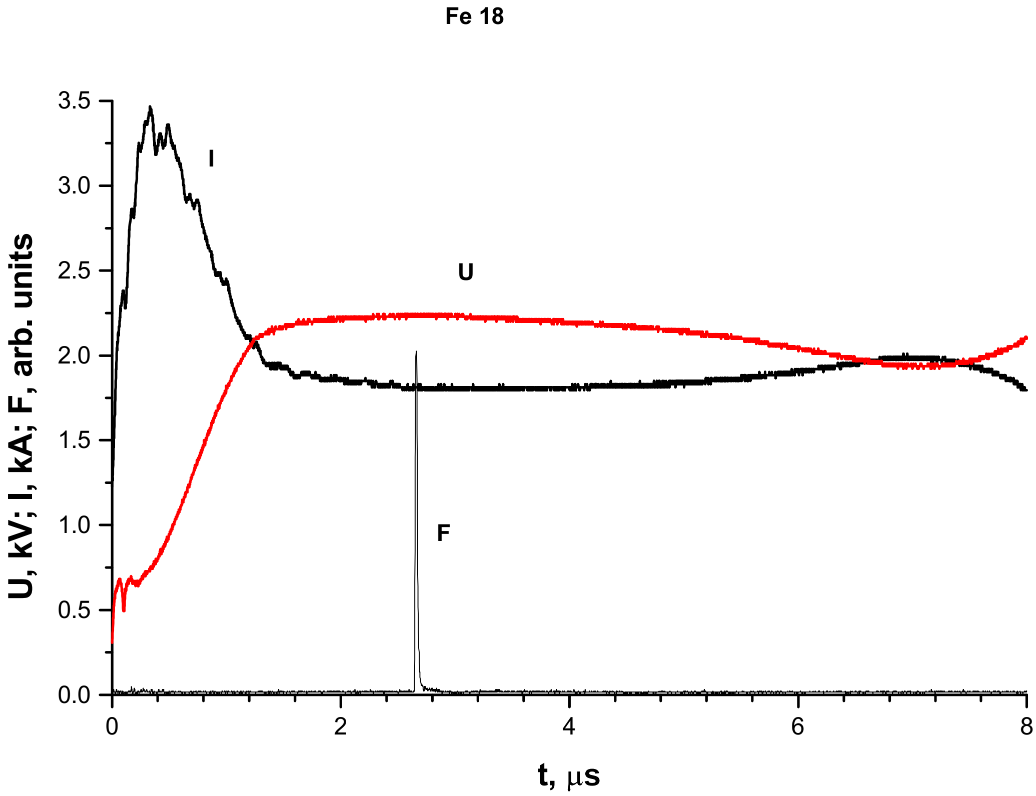

Fig.4

Initial experimental data (current I and voltage U against time) for one of our experiments.

Laser flash (F) is shown, just at the end of Fe melting (1.33 kJ/g according to [1]).

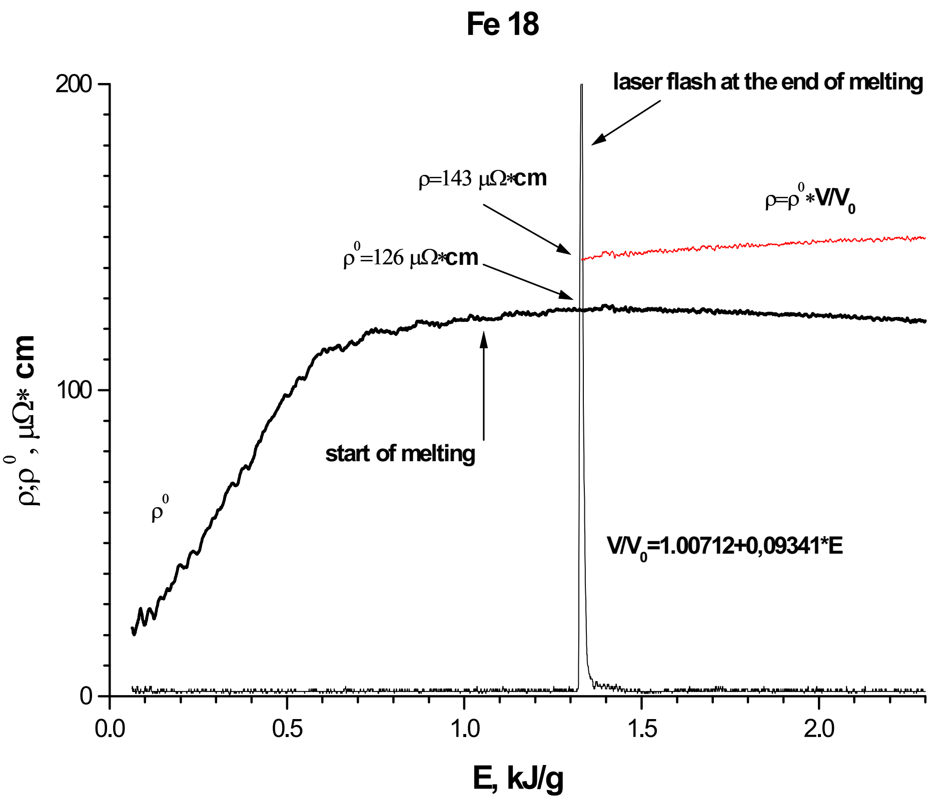

Fig.5

Electrical resistivity of Fe against specific imparted energy.

ρ^0 - electrical resistivity referred to initial dimensions of the specimen (126 μΩ*cm for liquid phase at melting point).

$\rho = \rho^0 \times V/V_0$ - electrical resistivity with thermal expansion taken into account (143 μΩ*cm for liquid phase at melting point). Volume dependence V/V_0 against E is shown.

Experimental data on liquid iron had been obtained in [5] by a fast electrical pulse heating under high argon pressure (2 kbars). Data on density were obtained up to 3950 K (E = 3.0 kJ/g). These data are shown in Fig.3. According to [5] average volume expansion coefficient $\beta = 93\times10^{-6}$ (near density of $\gamma = 7.1$ g/cm^3), $\beta = 115\times10^{-6}$ (near density of $\gamma = 5.7$ g/cm^3). Specific heat capacity is 0.815 kJ/g*K [5].

The steady-state experimental data was published [3] on the density of liquid iron at temperatures up to 2300 K. The data had been obtained by means of γ-densitometer. Within the temperature range of 1810 – 2300 K the density of liquid iron turned out to be a linear function of temperature. At the melting point the density of iron, as to [3] data, is about 7 g/cm^3, and at the temperature 2300 K it is about 6.7 g/cm^3. The average temperature coefficient of volumetric expansion of liquid iron is $\beta = 91{,}4\text{x}10^{-6}$ K^{-1}.

4. MEASUREMENTS ON LIQUID ZIRCONIUM

4.1. Review of Publications.

According to [7], an approximated equation to calculate density γ of liquid zirconium "at different temperatures" was proposed in 1956 [8]:

$$\gamma = 6.0 - (T - 2123)\times10^{-3} \text{ (g/cm}^3\text{)}$$

The [7] does not indicate up to what temperatures this dependence is true. The authors [7] indicated, that the result (6.06-6.08 g/cm^3) was given "at the temperature close to the melting temperature" for zirconium contained 0.5% of carbon. According to [9] recommendations, the density of liquid zirconium at the melting point equals to 5.95 g/cm^3. In 1983, the expansion of liquid zirconium (wire of 1 mm in diameter) was measured [10] under pulse heating. The author terms those measurements as preliminary. The measurements were done in a high-pressure vessel (3 kbar). The environs composition was not given. The measurement technique was the illumination by either laser or spark or X-ray; it was not specified. In case of a single experiment, the dependence of the expansion of zirconium on the imparted energy was obtained (Fig.6). For the solid phase of zirconium, the average linear thermal expansion coefficient α = 7.5×10^{-6} K^{-1} (300-1000 K)[11] and $\alpha = 8.0\times10^{-6}$ K^{-1} (T = 593-1093 K) [12].

4.2. Measurement Results on Liquid Zirconium Density

The measurements carried out for liquid zirconium (similarly to the measurements with regard to liquid iron) produced the following result (Fig.6). Fig.6 shows the ratio of the specific volume of zirconium to its initial specific volume V/V_0 depending on the specific imparted energy E. The square hollow dots and fitted curve represent our data. The curve we obtained is slightly below than that of the [10] data. According to our data (Fig.6), at the start of liquid state ($E \cong 0.85$ kJ/g) the expansion V/V_0 is ~ 5.7%, as in [10] it is 7%. During melting ($E_1 \cong 700$ J/g and $E_2 \cong 850$ J/g) the volume increases only 1.2%, while the review [9] recommends 5%. It should be mentioned for comparison that the expansion of iron at melting is 3% according to our data obtained by the same technique. The published data provides from 1 to 3.5 % in case of iron at the melting point. For the two points mentioned above (E = 0.85 kJ/g and E = 2.0 kJ/g) the density of liquid zirconium is 6.12 g/cm^3 and 5.55 g/cm^3 respectively (Fig.7).

5. DISCUSSION

According to our estimations the conditions of Zr wire being heated by electrical current within ~7 μsec up to the energies of ~2 kJ/g (the duration of heating up to melting is ~3 μsec) change as follows. In the course of heating, the thermal stresses occur to the specimen, which disappear toward the wire radius within ~25 nsec.

A sound wave covers the distance between the centre of a wire section and its ends within about 4 μsec that exceeds the period of time necessary to heat up to the melting.

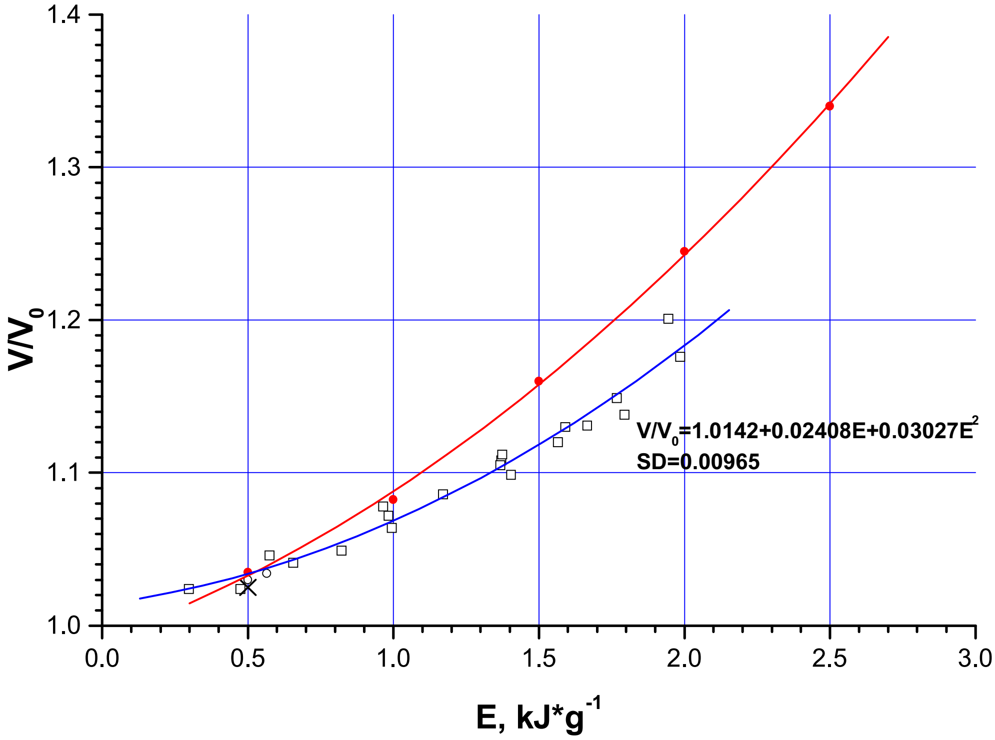

Fig.6

V/V_0 against imparted energy for zirconium.

Square hollow points and polynomial fit - our data. Standard deviation (SD) is shown. Circle solid points and polynomial fit - the part of [10] data. Two circle hollow points near 0.5 kJ/g - [13]. Cross under imparted energy 0.5 kJ/g - [12].

Therefore, the wire is compressed along its axis (at the imaging point equally distant from the ends). The estimation of stresses which may occur by the moment, when Zr is imparted with energy of 0.5 kJ/g, provides for the value of about 10-30 kbar that exceeds Zr yield limit (~2.8 kbar). Thus, the metal plastically deforms and expands along the wire radius. Such behaviour of the heated wire allows measuring the specific volume of solid zirconium, as well as the liquid one, by measuring the wire diameter only. It is quite natural that the cylindrical shape of the specimen is distorted (under such kind of deformation) that leads to non-uniform heating of metal and errors in measuring of resistivity and energy. The deviations of temperature will be of order of the wire cross-section variation. The described picture of deformation will take place in case there is no bend deformation. The bend deformation should lead to different displacement of the shadowgraph boundaries with regard to the wire central axis. In all our experiments, except for one, the displacement of boundaries is the same. This single experiment gives the displacement difference of 1-2 μm (at the energy of 1.67 kJ/g). This confirms the assumption, that the bend deformation is either absent or negligible. According to our data (Fig.6), at the specific imparted energy of E = 2.0 kJ/g the relative expansion of zirconium V/V_0 does not exceed 19%. To introduce the temperature value, we will use the data of J.K.Fink [15] for Zr (Enthalpy H = 1.78 kJ/g for T= 4200 K). Using these data, it is possible to calculate the average expansion coefficient of liquid zirconium (from the melting point up to 4200 K). In our experiment it turned out to be equal $\beta \cong 46\times10^{-6}$ K^{-1}.

According to the monograph [11] data, the temperature coefficient of linear expansion of iron (solid phase) α equals to ~ 20×10^{-6} K^{-1} before melting. According to the published data [11] for zirconium, the α equals to ~ 10×10^{-6} K^{-1} at 1600 K.

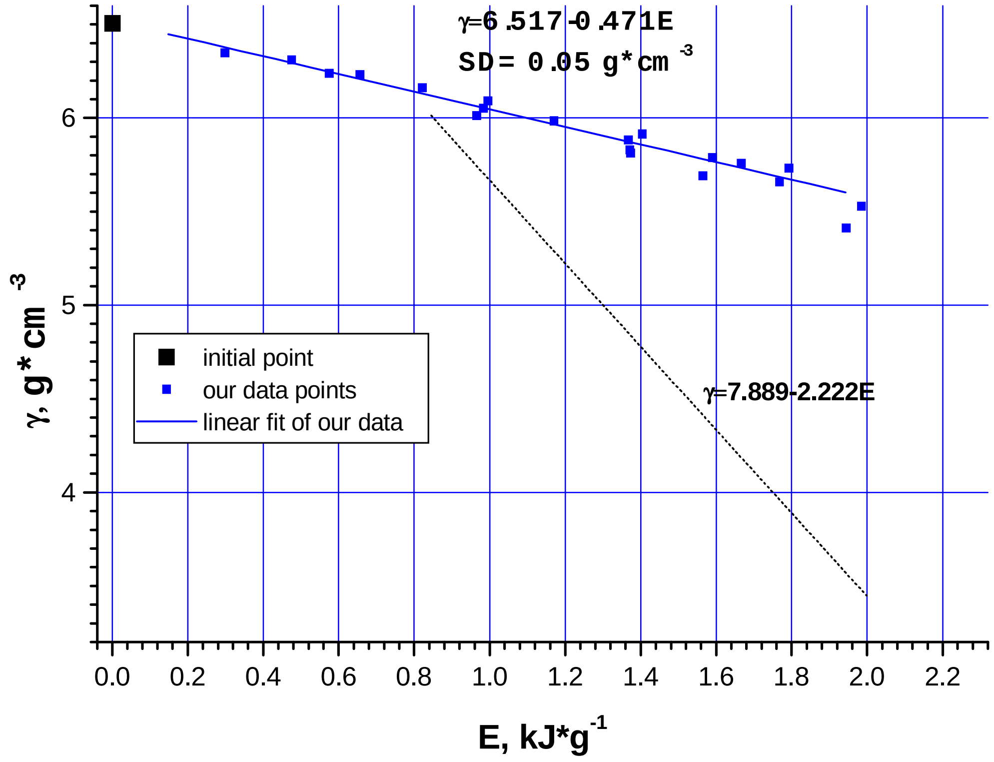

Fig.7

Density against imparted energy for solid (up to ~0.7 kJ/g)

and liquid (above ~0.85 kJ/g) zirconium.

Square points - our data, with the linear fit. Standard deviation (SD) is shown.

Dotted line - estimation of [7] for liquid Zr.

In other words, iron as in the solid state as in the liquid state has higher values of α and, correspondingly that of β.

According to our experimental data and evaluations, the average temperature coefficient of volumetric expansion of liquid iron β is ~ 102×10^{-6} K^{-1}, and for liquid zirconium it is ~ 46×10^{-6} K^{-1}.

Our results on liquid iron density are reasonably in line with the published data for other literature data for this liquid metal. Our results on the liquid zirconium density were obtained through direct density measurements (digital photometrical processing of the shadow picture across the wire), just as for experimental results for iron.

ACKNOWLEDGMENTS

This work was performed under the auspices of the International Nuclear Safety Centre of the Russian Minatom (RINSC) and the U.S. International Nuclear Safety Centre (USINSC) at the Argonne National Laboratory. Funding for this effort was provided by the US Department of Energy. The authors would like to thank Dr. Joanne K.Fink (physicist of Argonne National Laboratory) for useful discussions and for the interest to the investigations.

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